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(54) IMPROVEMENTS IN AND RELATING TO HIGH VOLTAGE INSULATING MATERIALS

(71) We, RAYCHEM LIMITED, a British Company, of Moor House, London Wall, London, E.C.2, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to high-voltage insulating materials.

Whilst polymeric materials are widely used for insulating a wide variety of electrical apparatus, they are not suitable for high voltage applications in contaminated atmospheres where moisture or fog, together with salts, dust particles and ionic pollution, cause leakage currents to flow across the surface of the insulation. This current causes a rise in temperature with consequent moisture evaporation and ultimately dry band formation. The electrical stress across these dry bands often exceeds the breakdown stress of the air-insulation interface, so that discharge or spark scintillation takes place. The spark temperature is extremely high, often 2000°C or higher, and the heat produced may be

sufficient to cause degradation of the insulation surface with the ultimate formation of carbonaceous spots. These carbonaceous spots usually link up in dendritic fashion and the organic insulation fails by progressive creepage tracking.

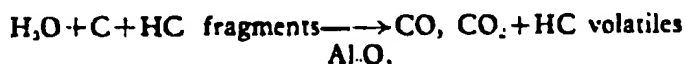
Over the years many solutions to these problems have been proposed of which perhaps the most effective has been the incorporation of hydrated alumina, preferably the trihydrate, in fairly substantial quantities to for example butyl rubber, epoxy resins, especially of the cycloaliphatic type, and, more recently, to ethylene-propylene rubbers.

There are several suggested modes of operation for this system as follows:

(a) Chemical action

The high arc temperatures cause degradation of the polymer system and simultaneously cause the filler to release the water of hydration.

The carbon and hydrocarbon fragments formed in the degradation of the polymer then react with the water in the presence of the aluminium oxide



The degradation products are thus removed from the insulation in gaseous form.

(b) Physical Action

The sudden increase in volume resulting from the conversion of the hydrate water into steam causes an explosion on the surface of the organic insulator which ejects carbon or dust particles, thus exposing or regenerating a clean unpolluted surface.

(c) Volume Effects

If a sufficient volume of filler is present the polymer is distributed as very thin layers between the filler particles and hence it would be difficult for the carbon that is produced under scintillation conditions to link up to form dendritic tracks. For this to happen very large volumes of fine particle fillers would be required and whilst this type of mechanism can be demonstrated to some extent, the brittle

resulting materials are extremely weak and

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(d) Thermal Effects

It has been postulated that the formation of steam, with the high latent heat of vaporisation will absorb sufficient energy to keep the organic material relatively cool and undegraded.

Whatever the correct mechanism, it is found in practice that polymeric materials containing large proportions of alumina trihydrate are substantially protected against tracking and usually fail only by progressive surface erosion.

The amount of alumina hydrate required to produce the anti-tracking effect is very high, however, and is usually in the region of 50—90% by weight of the entire insulation. In the case of polymers that can be shaped by moulding or extrusion, the high filler content causes undesirable characteristics

(i) During the shaping operation, which can involve temperatures up to 200°C or higher, the alumina hydrate starts to lose some of its water of hydration, which at such temperatures produces steam, which in turn leads to porous products. This must be avoided at all costs, since any voids or holes in an insulation material may produce catastrophic failure by corona discharge erosion on the inside of the void, which ultimately enlarges until failure occurs. At sufficiently high voltages, failure is extremely rapid and may be complete in a few seconds.

(ii) In the case of articles that are cross-linked after the shaping operation, especially by the use of high energy radiation of, for example, β or γ rays, the radiation can cause radiolysis of the hydrate to occur such that water is produced. This water appears to stay absorbed in the polymer/filler mixture until subsequently heated e.g. for expansion or distortion purposes or in service, when foaming occurs. Such a foam (if a lot of filler is radiolysed) or even the formation of a few small blisters has the same catastrophic effect as the porosity described in (i).

(iii) In the case of heat-shrinkable articles, the heat required to operate the shrinking process at an economic rate is high enough to cause loss of the hydrated water. If the shrinking temperature is very high this loss of water may cause porosity, and, even if no porosity is produced, the loss of any water reduces the performance of the polymeric insulation under polluting conditions.

Thus it is highly desirable to eliminate or greatly to reduce the porosity of void formation or loss of water which occurs when using alumina hydrate loaded materials.

The present invention provides insulating

material which is especially suitable for high voltage applications and which comprises a polymeric material and an anti-tracking filler system comprising at least 25% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of alumina trihydrate and from 3 to 20% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of a chemically treated silica filler, as hereinafter defined.

The alumina trihydrate will generally be present in an amount in the range of from 25 to 70% by weight of the polymeric material and the anti-tracking filler system but higher proportions may be used, especially when the insulation material is not intended to be given the property of heat-recoverability. The preferred percentage of hydrate will vary according to the polymeric material into which it is incorporated (since some polymers have a greater tendency to track than others) and also according to the environment in which the insulation is to be used. However, it can readily be determined by experiment and is in general advantageously within the range of from 40 to 70%, especially from 40 to 65%, by weight, of the polymeric material and the anti-tracking filler system.

Similarly the amount of the treated silica filler may vary over the range of from 3 to 20% by weight based on the weight of the polymeric material and the anti-tracking filler system, amounts falling within the range of from 4.5 to 10%, especially from 5 to 8%, being preferred.

By a "chemically treated silica filler" there is herein meant a filler comprising an inorganic silicon-containing compound containing the Si—O—Si group which has been treated with one or more silanes. Such chemically treated silica fillers and their preparation and properties are fully described in Patent Specification No. 1,284,081, the disclosures of which are incorporated herein by this reference. A brief summary of these chemically treated silica fillers and their preparation will, however, now be given:

The inorganic silicon-containing filler is typically a silica or silicate normally regarded as a reinforcing filler and having a specific surface area, measured by the Brunauer, Emmett and Teller nitrogen absorption method, of at least 50 m²/g. The filler may be anhydrous, i.e. containing less than 3.5% bound water, hydrated or an aerogel (prepared, for example, as described in Bachman et al, Rubber Reviews 1959, issue of Rubber and Chemistry and Technology).

To prepare the chemically treated fillers the inorganic silicon-containing fillers are treated with one or more silanes. The treatment may be carried out in a number of ways. For example the filler may be contacted with a gaseous silane, for example, dimethyl

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dichloro silane, at elevated temperatures, or the filler and silane may be mechanically mixed and the mixture stored until coating is complete, the time taken for the completion of the coating being in the range of one day to several weeks depending on the temperature. However, the method of treating the filler with the silane is not critical for the present invention. The filler is advantageously coated with the silane to the extent of one monolayer, although fillers of which a lower proportion of the surface is coated with silane may also be used in the present invention.

As silanes there are especially preferred substituted silanes of the formula



wherein n is 1, 2 or 3, R represents an organic radical bonded to the silicon atom by a Si—C bond and X represents a radical bound to the silicon atom via an atom other than a carbon atom. Amongst suitable compounds are, for example, methyl trichlorosilane, dimethyl dichlorosilane, trimethyl chlorosilane, vinyl trichlorosilane, γ - methacryloxy - propyl - trimethoxysilane and its hydrolysis products, γ - methacryloxypropyl - triethoxy silane and its hydrolysis products, N,N - bis(β - hydroxyethyl) - γ - amino - propyl - triethoxy silane and its hydrolysis products, vinyl triethoxy - silane and its hydrolysis products, γ - glycidoxo - propyl - trimethoxysilane, γ - mercaptopropyl - trimethoxy silane and its hydrolysis products and vinyl trimethoxy silane. Dimethyl dichlorosilane, trimethyl chlorosilane, γ - glycidoxo - propyl - trimethoxysilane, vinyl triethoxy silane, γ - methacryloxy - propyltrimethoxy silane and γ - methacryloxy - propyl - triethoxy silane are especially preferred for the preparation of chemically treated silica fillers suitable for use in the present invention.

The presence of functional organic R groups in the silanes makes it possible to control the compatibility and/or the reactivity of the chemically treated silica fillers with various polymers.

It has surprisingly been found that the chemically treated silica fillers substantially reduce or eliminate porosity during processing. As they are hydrophobic, they cannot be expected to absorb water released from the inorganic hydrate. Without in any way wishing to limit the present invention by theory, it is possible that they reinforce the polymeric composition and raise its modulus thus preventing the expansion which is essential if pores are to be formed. Alternatively they may act as lubricants, thereby reducing heat build-up during processing or effecting uniform dispersions of the inorganic hydrate. Even more surprisingly they have also been

found to increase the anti-tracking properties of the system.

Amongst polymers into which the anti-tracking filler system may suitably be incorporated there may be mentioned, for example, polyethylene, polypropylene, ethylene/propylene copolymers, ethylene/propylene/non-conjugated diene terpolymers (e.g. those sold by U.S. Rubber Corporation under the trade name "Koyalene"), ethylene copolymers, for example, with ethyl acrylate or vinyl acetate, chlorosulphonated polyethylene, chlorosulphonated polypropylene, silicone rubbers as well as mixtures of two or more such polymers.

Especially useful insulation materials of the present invention are cross-linked and, preferably, imparted with the property of heat-recoverability. For example, it may be in the form of heat-shrinkable tubes, udders and sheds for use in cable connexions or heat shrinkable end-caps for cable terminations. The present invention therefore also provides shaped articles comprising the insulation material of the present invention which articles may, if desired, be in a heat-recoverable form.

The present invention also provides a mouldable or extrudable composition suitable for processing into the insulating material of the present invention.

The insulating materials and compositions of the present invention may, if desired, contain other fillers, for example, flame retardants, reinforcing fillers, pigments and mixtures thereof.

The anti-tracking filler system can be incorporated into the polymer(s) by any of the commonly used techniques, for example, in a twin-roll mill at elevated temperatures. Similarly the resulting compositions can readily be processed into sheets of material or other shaped articles by any of the usual methods.

The insulation materials of the present invention are especially useful in high-voltage applications, for example, at voltages up to 11KV or even higher. It will be appreciated that although the primary purpose of the anti-tracking filler is to prevent creep-tracking as outlined above, the materials will also be effective in stabilising the insulation under arcing conditions i.e. in cases where a direct arc passes between two parts of an electrical apparatus forming a carbonaceous track along its line. This phenomenon is slightly different from creep-tracking where, for example, conducting contaminants and/or surface irregularities cause a leakage current and a tree-like carbonaceous path develops on the surface of the insulation.

It will be understood, however, that the invention is not limited to any particular application and also that it is not in any way to be limited by the proposed theoretical

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4 explanation of the mechanism of action of the anti-tracking system.

The following Examples illustrate the invention:

EXAMPLES 1 to 3

5 The following formulations were prepared on a twin roll mill at about 110°C:—

	Example 1	Example 2	Example 3
10 Ethylene - propylene - dicyclopentadiene terpolymer	130	100	130
Ethylene - ethyl acrylate copolymer	—	30	—
Low density polyethylene (M.F.I. 3.0)	40	40	40
Polymerised tetra hydro quinoline anti- oxidant	8	8	8
15 Ferric oxide (pigment)	20	20	20
Chemically treated silica filler	20	20	20
Alumina trihydrate	150	150	200
Triallyl cyanurate	2	2	2

20 The chemically treated silica filler consisted of a silica aerogel coated with dimethyl dichloro silane to approximately one monolayer. This filler had a specific surface area of approximately 150 sq.m/g (BET method) and an average particle size of 20 μ .

25 These formulations were extruded into tubing of internal diameter 1.0 in. and wall thickness 0.110 in. at temperatures up to 150°C (at the extruder die) with good surface finish and no porosity.

30 By way of comparison a similar control formulation was prepared which was identical to the formulation of Example 1 except that no filler additive was present and this, when extruded as before, produced tubing of rough surface appearance and some internal bubbles and it was not possible to eliminate the bubbles present in the tubing by varying extrusion conditions.

40 All these formulations were again prepared and pressed into plaques 5×2×0.25 in. and irradiated under nitrogen with γ -rays to a dose of 15 Mrads. These plaques were then tested according to ASTM D2303 which measures the tracking and erosion resistance of polymeric insulators by the liquid contaminant inclined plane method. The time to track 1 inch at 6 KV using a contaminant of 0.1% ammonium chloride solution with 0.1% glycerol-ethylene oxide condensate as non-ionic wetting agent was determined. The resistivity of this solution was 380 ohms-cm at 23°C and the rate of application of contaminant was 0.9 ml/min. The results were as follows:

55 Experiment	Time to track 1 inch at 6 KV (mins)
Control	42
1	770
2	>1000
60 3	>1000

These results demonstrate the remarkable improvement in tracking resistance and lack of

porosity conferred by the addition of the chemically treated silica filler.

WHAT WE CLAIM IS:—

1. Insulating material which is especially suitable for high voltage applications and which comprises a polymeric material and an anti-tracking filler system comprising at least 25% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of alumina trihydrate and from 3 to 20% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of a chemically treated silica filler, as hereinbefore defined.

2. Insulating material as claimed in claim 1, which comprises from 25 to 70% by weight, based on the weight of the polymeric material and the anti-tracking filler system of alumina trihydrate.

3. Insulating material as claimed in claim 2, which comprises from 40 to 70% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of alumina trihydrate.

4. Insulating material as claimed in claim 3, which comprises from 40 to 65% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of alumina trihydrate.

5. Insulating material as claimed in any one of claims 1 to 4, which comprises from 4.5 to 10% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of the chemically treated silica filler.

6. Insulating material as claimed in claim 5, which comprises from 5 to 8% by weight, based on the weight of the polymeric material and the anti-tracking filler system, of the chemically treated silica filler.

7. Insulating material as claimed in any one of claims 1 to 6, wherein the chemically treated silica filler has been coated with a silane to a depth of about 1 monolayer.

8. Insulating material as claimed in any

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one of claims 1 to 7, wherein the chemically treated silica filler is one which has been treated with a silane of the formula



5 wherein n is 1, 2 or 3, R represents an organic radical bonded to the silicon atom by a Si—C bond and X represents a radical bound to the silicon atom via an atom other than a carbon atom.

10 9. Insulating material as claimed in claim 8, wherein the silane is dimethyldichlorosilane, trimethylchlorosilane, γ -glycidoxypropyl-trimethoxysilane, vinyl ethoxy silane, γ -methacryloxy-propyltrimethoxy silane or

15 γ -methacryloxy-propyl-triethoxy silane.

10. Insulating material as claimed in any one of claims 1 to 9, wherein the polymeric material comprises polyethylene, polypropylene, an ethylene/propylene copolymer, and ethylene/propylene/non-conjugated diene terpolymer, an ethylene/ethyl acrylate copolymer, an ethylene/vinyl acetate copolymer, a chlorosulphonated polyethylene, a chlorosulphonated polypropylene, a silicone rubber or a blend of any two or more of said polymers.

25 11. Insulating material as claimed in claim

10, wherein the polymeric material is cross-linked.

12. Insulating material as claimed in any one of claims 1 to 11, wherein the polymeric material is heat-recoverable. 30

13. Insulating material as claimed in any one of claims 1 to 12, which comprises a flame-retardant, a reinforcing filler, a pigment or a mixture of two or more said substances. 35

14. Insulating material as claimed in claim 1, substantially as described in any one of Examples 1 to 3 herein. 40

15. An electrical component which is insulated by insulating material as claimed in any one of claims 1 to 14.

16. An electrical component as claimed in claim 15, which is a high voltage cable or cable termination. 45

17. A mouldable or extrudable composition suitable for processing into insulating material as claimed in any one of claims 1 to 14.

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